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AT BE DE FR GB IT LU SE(71) Applicant: **THE FIRESTONE TIRE & RUBBER COMPANY**
1200 Firestone Parkway
Akron, Ohio 44317(US)(72) Inventor: **Kang, Jung W.**
6150 Terrace Hills Drive
Clinton Ohio 44216(US)(72) Inventor: **Davis, James A.**
10688 Mogadore Road
Uniontown Ohio 44685(US)(74) Representative: **Kraus, Walter, Dr. et al,**
Patentanwälte Dres. Kraus & Weisert Irmgardstrasse 15
D-8000 München 71(DE)(54) **Cured rubber skim stock compositions having improved metal adhesion and metal adhesion retention.**

(57) This invention is directed toward a rubber skim stock composition and a product containing the skim stock having improved adhesion and adhesion retention with metallic reinforcement cords such as brassed steel. The invention composition comprises a vulcanizable rubber skim stock and an organic complex of cobalt or nickel with a dicarboxylic acid and is prepared by mixing the cobalt or nickel complex with the rubber skim stock prior to contacting the metallic reinforcement. Tests conducted with brass-plated steel cords showed satisfactory and improved metal adhesion, percent rubber coverage and metal adhesion retention with use of the rubber skim stock of this invention when compared to existing formulations containing known adhesion promoting cobalt additives.

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CURED RUBBER SKIM STOCK COMPOSITIONS
HAVING IMPROVED METAL ADHESION AND
METAL ADHESION RETENTION

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Technical Field

The present invention is directed toward improvement in the adhesion and adhesion retention between a rubber skim stock composition, used in the manufacture of tires, conveyor belts, hoses and the like, and metallic reinforcement cord such as steel wire and cable which commonly carries a protective coating of zinc or brass. Improved adhesion and adhesion retention result when a metal complex of a dibasic acid is present in the rubber skim stock composition.

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In the manufacture of the foregoing rubber articles, particularly steel-belted bias and radial tires, it has become common to reinforce the rubber skim stock material with steel wire or cable. The metallic reinforced rubber is employed as a belt, one or more of which is circumferentially oriented beneath the tread stock to maintain the integrity and shape of the tire during inflation and subsequent load. In order for the belt to function effectively, it is imperative that adhesion between the rubber and the steel cord be effectively maintained. Because steel is prone to oxidation, which even in minor degree is highly deleterious to the necessary adhesion with the rubber skim stock, and it would be most impractical to incorporate a chemically clean, oxidation-free steel cord in the belt at the time of its manufacture, the steel cord is plated with zinc or brass thereby protecting it from oxidation until it can be used.

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While adhesion between zinc or brass-plated steel cord and rubber is generally far greater than that between the latter and oxidized steel, existing data determined from article life as well as modern testing techniques indicates that adhesion obtained between plated steel cord and the elastomer must be increased for improved article

life and service. Adhesion must also be improved between the rubber skim stock and bright steel, i.e., surfaces of the cord which are neither plated nor oxidized, generally occurring when the steel cords and rubber skim stock are cut to size from larger, calendered sheets of the reinforced rubber stock.

Background Art

In order to promote adhesion between rubber and ferrous metals it is known to employ a variety of metallic salts as coatings to the metal or as an ingredient in a rubber composition. One early patent embodying the former technique is U.S. Pat. No. 1,919,718 which discloses a composite rubber product that adheres to ferrous metals. The invention requires the coating of the metal with a metallic salt such as that formed with copper, cobalt, manganese, iron or lead and a fatty acid of high molecular weight, e.g., stearic, palmitic, oleic, linoleic, lauric and the like. Alternatively, the metallic salt may be dissolved in a solvent or in a rubber cement which is then applied to the metal surface. The rubber layer is then applied and vulcanized in position.

U.S. Pat. No. 2,643,273 discloses a rubber adhesive composition which contains a water soluble cobalt salt to increase the adherence of rubber to metal. The specification discloses incorporating cobalt chloride or sulfate in the rubber or dipping the metal in a solution of the salt.

U.S. Pat. No. 2,912,355 is directed toward improving the adhesion between rubber and metal by the incorporation into a rubber composition of a partially oxidized metal salt of an aliphatic fatty acid compound, the metal being cobalt, copper, iron, lead, mercury, nickel or silver.

U.S. Pat. No. 3,897,583 is directed toward the adhesion of metal to rubber by incorporating a cobalt salt in a rubber stock which contains an adhesive resin forming

system based on a methylene donor which is a methyolated nitroalkane in combination with a resorcinol type methylene acceptor. Cobalt salts disclosed include those of aliphatic or alicyclic carboxylic acids having 6-30 carbon atoms.

U.S. Pat. No. 3,903,026 discloses a rubber composition containing cobalt carboxylate and magnesium oxide to improve the adhesion of the rubber to zinc or zinc alloy plated steel.

U.S. Pat. No. 3,936,536 discloses the method of adhering rubber to metal by coating the metal with rubber containing a small amount of $\text{Co}(\text{NH}_3)_2 \cdot \text{Cl}_2$.

U.S. Pat. No. 3,993,847 discloses a process of bonding a rubber to a ferrous metal and such a laminated article. Adhesion is improved by employing an adhesive comprising a conjugated diene and a heterocyclic nitrogen base and containing about 5-180 parts of silica filler per 100 parts of the diene-heterocyclic nitrogen interpolymers. The patent states that adhesion is further improved by using a rubber containing small amounts of cobalt metal.

Thus, while others have sought to enhance adhesion between rubber compositions and metals by employing certain metallic salts and complexes, including monocarboxylate complexes, with or without other compounds such as resins, the art of which we are aware has not disclosed the use of metal dicarboxylic acid complexes in rubber skim stock compositions to improve rubber-to-metal adhesion and adhesion retention in cured skim stocks and articles such as tires.

Disclosure of Invention

The cured rubber skim stock compositions of the present invention comprise 100 parts of a vulcanizable rubber stock and from about 0.50 to about 10.0 parts by weight of an organic complex of cobalt and a dicarboxylic acid per 100 parts of the rubber component in the rubber stock or, from about 0.50 to about 12.0 parts by weight

of an organic complex of nickel and a dicarboxylic acid per 100 parts of the rubber component in the rubber skim stock. Aliphatic and aromatic dicarboxylic acids having from two to about 20 carbon atoms can be employed to form the
5 complex. The use of these metal complexes in a rubber skim stock provides improved metal adhesion and metal adhesion retention properties with metallic reinforcing cord particularly brass-plated steel cord.

A tire having metallic reinforcing elements
10 embedded in vulcanized rubber skim stock is also provided, the skim stock being characterized by having incorporated therein from about 0.50 to about 10.0 parts by weight of an organic complex of cobalt and a dicarboxylic acid per 100 parts of the rubber component in the rubber skim stock
15 or, from about 0.50 to about 12.0 parts by weight of an organic complex of nickel and a dicarboxylic acid per 100 parts of the rubber component.

Preferred Mode for Carrying Out the Invention

20 To illustrate our invention, a typical rubber skim stock is presented hereinbelow which is suitable for preparation of rubber articles such as tires. Adhesion between this stock with steel reinforcement subsequent to vulcanization has been measured and is also presented
25 hereinbelow. It is to be understood that the composition of the rubber skim stock provided is not part of the present invention and that it has been presented solely to enable those skilled in the art to have at least one rubber skim stock with which to practice the invention.

30 The ingredients utilized in the practice of the present invention include organic complexes of the metals with dicarboxylic acids, having from two to about 20 carbon atoms. The complexes are prepared by the combination of the metal hydrate and the dicarboxylic acid. Suitable
35 aliphatic dicarboxylic acids used to practice the present invention would be oxalic, malonic, maleic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic,

citric and the like. Suitable aromatic dicarboxylic acids would be phthalic, isophthalic, terephthalic, hemimellitic, trimellitic, homophthalic, o, m and p-phenylenediacetic, o-phenyleneacetic- β -propionic and the like. As is understood by those skilled in the art, the dicarboxylic acids are also commonly referred to as dibasic acids. The metal used to prepare the complex of the dicarboxylic acid could be selected from the group consisting of cobalt, nickel, copper, barium, iron, mercury, tin, zinc, calcium, magnesium and silver, with cobalt and nickel being preferred.

Particularly useful as the cobalt complexes are cobalt adipate and cobalt azelate both of which are prepared from the corresponding acid and cobalt hydroxide. Cobalt adipate, as used in the experimental work discussed hereinbelow, is a purple powder having about 28.5% cobalt and a specific gravity in kerosene of 3.928 ± 0.5 at 25° C. Cobalt azelate, as used in the experimental work discussed hereinbelow, is a purple powder having about 22% cobalt. Particularly useful as the nickel complex is nickel adipate prepared from adipic acid and nickel hydrate. Nickel adipate, as used in the experimental work discussed hereinbelow, is a green powder having 27% nickel content and a specific gravity in kerosene of 5.015 ± 0.5 at 25° C.

Amounts of the cobalt complex employed can range from about 0.50 to about 10.0 parts per hundred parts of rubber (phr) with 1.35 phr being preferred. Similarly, the amount of nickel complex employed can range from about 0.50 to about 12.0 phr with 1.40 phr being preferred. Other cobalt or nickel complexes of the foregoing dicarboxylic acids can be employed in substantially the same amounts.

In order to determine the improvement in adhesion obtained when the cobalt or nickel complexes are added to the rubber skim stock, T-adhesion tests (rubber-to-steel cord) were conducted according to the procedure which follows.

The test utilized T-adhesion pads prepared by placing 60 gauge slabs of uncured fully compounded rubber

skim stock on 51 gauge fabric reinforced rubber backing. Commercial brass-coated cables (1 x 5 x 0.25 mm diam.) were placed between two pads of the reinforced skim stock with the wires in contact with the uncured rubber skim at 1.25 cm intervals. The width of each adhesion pad was 1.25 cm. The pads were placed in a curing mold and were cured for 30 minutes at 149° C. Testing was done on a Model 1130 Instron Universal Tester at a crosshead speed of 25.4 cm per minute and 110° C. The T-adhesion pads were preheated in the 110° C oven for 20 minutes prior to testing. Oven aging of the cured T-adhesion pads was done in a forced air oven at 121° C for two days. Steam bomb aging of the cured samples was done in a pressure tight bomb for one hour at 149° C, in a saturated steam atmosphere.

Detailed T-Adhesion Test Procedure

1. Using a Clicker machine and a 15.24 x 1.25 cm die, prepare an adequate number of calendered and control stock samples of T-adhesion pad building.
2. Use one piece of calendered fabric reinforced rubber backing (0.1295 cm).
3. Ply one piece of 60 gauge control rubber stock (0.1524 cm) onto the fabric backing.
4. Place sample in building jig with fabric side down.
5. Place ten cords (of brass or zinc coated wire) approximately 17.78 cm in length equally spaced on top of the two piece assembly.
6. Invert another 2 ply assembly, made as in items 1, 2 and 3, on top of cords so that cords are between the two layers of rubber skim stock to be tested.
7. This assembly should now fit snugly into the cavity of the curing mold.
8. Adhesion pads shall be cured for 30 minutes at 149° C and then allowed to equilibrate for 24 hours before testing.
9. Testing Machine: Model 1130 Instron Universal Tester.
10. Test speed 25.4 cm/minute; testing temperature, 110° C after 20 minutes preheat.

11. The top grip shall be of a special holder made for the cured sample, with a slot in the bottom to permit the sample to be inserted with the wires protruding. The bottom grip should be a wedge type, designed to exert increasing tightening as each wire is pulled from the cured sample.
12. Record 10 wire pull-outs and average. Multiply average pull-out force value by 0.3572 to obtain kilograms per centimeter.

In the tests which follow, a rubber skim stock, Stock A, was prepared to which the ingredients of the present invention were added in varying amounts. Formulations for each are as follows with all parts given on the basis of parts per hundred parts of rubber (phr) by weight, unless otherwise specified.

Compounding Ingredients

Stock A

Natural Rubber

100

HAF carbon black

60

Zinc Oxide

7.5

Stearic Acid

0.5

Hydrocarbon resins

2.0

Santoflex DD*¹

2.0

NOBS Special*²

0.8

Santoflex 13*³

1.0

Process Oil

2.0

Sulfur MB*⁴

7.5

Santogard PVI*⁵

0.4

*1 6-dodecyl-1,2-dihydro-2,2,4-trimethylquinoline

*2 N-oxydiethylene benzothiazole 2-sulfenamide

*3 N-(1,3 dimethylbutyl)-N'-phenyl-p-phenylenediamine

*4 80% Insoluble sulfur and 20% process oil preblend

*5 N-(cyclohexylthio)phthalimide

In the first series of tests which follow, cobalt adipate and cobalt azelate were added to Stock A in amounts

of 1.35 and 1.75 phr, respectively. Rubber skim stocks containing cobalt adipate and cobalt azelate appear as Examples 3 and 4, respectively. For purposes of comparison, both complexes were evaluated against two other compositions, Examples 1 and 2, both of the latter consisting of Stock A, and a different cobalt additive known to improve rubber-to-metal adhesion and adhesion retention. All cobalt additives studied were individually incorporated into Stock A to give a concentration of 0.2 percent cobalt metal, based upon the total weight of the rubber skim stock. Example 1 contained 2.40 phr of a cobalt complex, Mooney Cobalt 401, a dark purple viscous liquid comprising about 15.5 to 16.5 percent cobalt. It has a viscosity (at 25° C) of 1000 to 9000 cps; a specific gravity of 1.10 to 1.20 and, an ash content of from 23 to 28 weight percent. Mooney Cobalt 401 is commercially available from Mooney Chemical, Inc., Cleveland, Ohio. Example 2 contained 2.40 phr of Manobond C-16 which is a commercially available source of a cobalt and boron containing additive having from 9 to 12 carbons. Manobond C-16 is available as a dark purple, viscous liquid; it contains 15.5 to 16.5 percent cobalt; it has a viscosity (at 25° C) of 3,000 to 9,000 cps and an ash content from 22 to 25 weight percent. Manobond C-16 is commercially available from Wyrough and Loser, Inc., Trenton, New Jersey. A control was also provided consisting of Stock A alone without any adhesion promoting additives.

Three sets of tests were conducted with the Control (containing no cobalt or nickel additives) and Examples 1-4 and these are reported in Table I. The tests included T-adhesion determination for vulcanized specimens -- unaged or unconditioned, Test A; oven aged, Test B; and, steam bomb aged, Test C. The force necessary to pull or remove the metallic reinforcement from the vulcanized rubber skim stock is given first, in kg/cm, followed by the percent of rubber skim stock remaining on the surface of the metallic reinforcement. The amount of rubber skim stock remaining on the metallic reinforcement was determined

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by visual examination and has been reported as % rubber
coverage. **0059883**

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TABLE I
Short Term Wire Adhesion Data Comparing Two Commercially
Available Cobalt Additives and Two Dicarboxylic Acid Complexes of Cobalt

	<u>Control</u>	<u>Ex. 1</u>	<u>Ex. 2</u>	<u>Ex. 3</u>	<u>Ex. 4</u>
Mooney Cobalt 401, phr	---	2.40	---	---	---
Manobond C-16, phr	---	---	2.40	---	---
Cobalt Adipate, phr	---	---	---	1.35	---
Cobalt Azelate, phr	---	---	---	---	1.75

Test A

Unaged or Unconditioned
Plated Steel Cord^a

Brass-plated					
Kg/cm	25.72	27.15	25.00	28.40	26.61
% rubber coverage	95-100	95-100	95-100	100	95-100
Zinc-plated					
Kg/cm	5.00	22.86	18.93	22.33	23.58
% rubber coverage	0	90	85	90-95	85-90

Test B

Oven Aged Plated Steel Cord^b

Brass-plated					
Kg/cm	18.22	18.61	18.11	18.04	23.58
% rubber coverage	90	95	90-95	95-100	90
Zinc-plated					
Kg/cm	1.79	22.61	18.29	17.32	14.65
% rubber coverage	0	75-80	70	80	80

TABLE I (Continued)

<u>Test C</u>	<u>Control</u>	<u>Ex. 1</u>	<u>Ex. 2</u>	<u>Ex. 3</u>	<u>Ex. 4</u>
Steam Bomb Aged Plated					
Steel Cord ^C					
Brass-plated	15.90	18.54	17.16	19.74	23.04
Kg/cm					
% rubber coverage	85	65-70	70	85	95-100
Zinc-plated					
Kg/cm	---	21.47	20.50	17.38	22.33
% rubber coverage	---	80	90	85-90	65

- a) T-adhesion pads cured 30 minutes at 149° C and tested at 110° C.
- b) T-adhesion pads cured 30 minutes at 149° C, heat aged in a forced air oven for 2 days at 121° C and tested at 110° C.
- c) T-adhesion pads cured 30 minutes at 149° C, steam bomb aged 1 hour at 149° C and tested at 110° C.

As can be determined from Table I, Test A, unaged adhesion of the control stock to brass-plated steel cord was significantly better than to zinc-plated steel cord. The addition of the cobalt complexes of the present invention (Examples 3 and 4) provided adhesion properties as good as or slightly better than reported for Examples 1 and 2 with both brass-plated cord and the zinc-plated steel cord.

In Test B, oven aging, adhesion of the stocks with the brass-plated wire was again comparable to the adhesion with the brass-plated wire with the cobalt complexes of the present invention, whereas with the zinc-plated wire properties were slightly lower. Of course, for the Control, adhesion with the brass-plated wire was significantly better than with the zinc-plated wire. The oven aging test is an accelerated heat aging test and is significant in determining the effect of heat on the thermal stability of the chemical bonds formed between the rubber skim stock and the metallic reinforcement during vulcanization.

In Test C, steam bomb aging, adhesion of the stocks of Examples 3 and 4 with brass-plated wire and zinc-plated wire was as good as and slightly better than the adhesion reported for Examples 1 and 2. Steam bomb aging for one hour at 149° C is an accelerated humidity aging test and is significant in determining the chemical stability of the chemical bonds formed between the rubber skim stock and the metallic reinforcement when exposed to moisture or steam under pressure.

In the second series of tests, reported in Table II, the effect of long term humidity chamber aging is presented for periods of time of 0-90 days between the Control, Stock A and Examples 1-3, with brass-plated steel cord and with zinc-plated steel cord. Ninety day long term humidity chamber aging data was not determined for zinc-plated steel cord. In addition to adhesion pull out force values, and percent rubber coverage values, also reported

are percent adhesion retention values. Percent retention is a determination of metal adhesion retention and is defined as follows:

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$$\text{Percent Retention} = \frac{\text{Adhesion Pull-Out Force of Aged Specimen}}{\text{Adhesion Pull-Out Force of Unaged Specimen}} \times 100$$

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TABLE II

Long Term Humidity Aging Wire Adhesion Data Comprising Two Commercially Available Cobalt Additives and a Dicarboxylic Acid Complex of Cobalt

	Control	Ex. 1	Ex. 2	Ex. 3
Mooney Cobalt 401, phr	---	2.40	---	---
Manobond C-16, phr	---	---	2.40	---
Cobalt Adipate, phr	---	---	---	1.35

Test D

0 Day Humidity Chamber Test

Brass-Plated Steel Cord^d

Kg/cm

% rubber coverage

Zinc-Plated Steel Cord^d

Kg/cm

% rubber coverage

Test E

30 Day Humidity Chamber Test

Brass-Plated Steel Cord^d

Kg/cm

% rubber coverage

% retention

Zinc-Plated Steel Cord^d

Kg/cm

% rubber coverage

% retention

27.54	27.15	25.00	28.75
95	95-100	95-100	95
2.14	22.86	18.93	24.47
0	90	85	95
24.29	25.72	23.22	30.54
90	100	100	95-100
88.2	94.7	92.9	106.2
---	16.07	14.11	24.49
---	55-60	25-30	95
---	70.3	74.5	100.1

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TABLE II (Continued)

Control	Ex. 1	Ex. 2	Ex. 3
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Test F

60 Day Humidity Chamber Test

Brass-Plated Steel Cord^d

Kg/cm

% rubber coverage

% retention

Zinc-Plated Steel Cord^d

Kg/cm

% rubber coverage

% retention

Test G

90 Day Humidity Chamber Test

Brass-Plated Steel Cord^d

Kg/cm

% rubber coverage

% retention

d) T-adhesion pads cured 30 minutes at 149° C, aged in humidity chamber at 90% relative humidity and 35° C and tested at 110° C.

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Tests D through G, representing the effect of humidity chamber aging, show that the control Stock A gradually lost adhesion properties with aging. The effect of humidity aging on Examples 1 and 2 indicated a loss of adhesion, comparable to that observed with the Control although, unlike the latter, the percent rubber coverage remaining on the metallic reinforcement was improved. Percent retention, i.e., metal adhesion retention discussed hereinabove, decreased with the Control and Examples 1 and 2. Addition of cobalt adipate to Stock A (Example 3) greatly improved the adhesion of the cured stock to brass-plated steel cord and it can be noted that the percent rubber coverage and adhesion retention values after 90 days of aging was still 90 and 91.0 percent, respectively. With respect to adhesion, percent rubber coverage and adhesion retention of the various stocks to zinc-plated steel cord, all values were significantly higher for Example 3 than Examples 1 or 2 and particularly the Control which was not even tested after the 0 day evaluation. Generally speaking, adhesion of cured skim stocks to brass-plated steel cord is more successful than to zinc-plated steel cord and therefore the values reported for Example 3 are unexpectedly good.

Significance of the humidity chamber tests is again in determining the chemical stability of chemical bonds formed between the rubber skim stock and the metallic reinforcement when exposed to conditions of high relative humidity and high temperature, as compared to ambient, and extended periods of time.

Having established that favorable short term and long term adhesion properties could be obtained with cobalt complexes of dicarboxylic acids, we next varied the metal by employing a nickel complex specifically, nickel adipate. The test results are reported in Table III which provides short term adhesion and long term humidity aging adhesion values for two examples -- Example 5, consisting of Stock A and 2.0 phr of Manobond C-16, and Example 6 consisting

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of Stock A and 1.40 phr of nickel adipate. A separate control was not run with these tests inasmuch as adhesion values had previously been determined with evaluation of the cobalt complexes reported hereinabove. The nickel complex provided no adhesion between the rubber skim stock and zinc-plated steel cord and therefore no values are reported. For adhesion to zinc-plated steel cord, a cobalt complex should be employed.

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TABLE III
Short Term and Long Term Humidity Aging
Data with Nickel Adipate Complex

	<u>Ex. 5</u>	<u>Ex. 6</u>
Manobond C-16, phr	2.0	---
15 Nickel Adipate, phr	---	1.40

Test A

Unaged or Unconditioned
Plated Steel Cord^a

20 Brass-plated		
Kg/cm	29.47	25.90
% rubber coverage	95-100	95

Test B

Oven Aged Plated Steel Cord^b

25 Brass-plated		
Kg/cm	14.65	15.00
% rubber coverage	95	90-95

Test C

Steam Bomb Aged Plated
Steel Cord^c

30 Brass-plated		
Kg/cm	13.75	16.43
% rubber coverage	65-70	80

Test D

0 Day Humidity Chamber Test
Brass-Plated Steel Cord^d

35	Kg/cm	28.75	25.00
	% rubber coverage	95	90

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TABLE III (Continued)

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		<u>Ex. 5</u>	<u>Ex. 6</u>
	<u>Test E</u>		
5	30 Day Humidity Chamber Test		
	Brass-Plated Steel Cord ^d		
	Kg/cm	27.33	21.61
	% rubber coverage	95	90
	% retention	95.0	86.4
10	<u>Test F</u>		
	60 Day Humidity Chamber Test		
	Brass-Plated Steel Cord ^d		
	Kg/cm	28.04	25.18
	% rubber coverage	90-95	90-95
15	% retention	97.5	100.7
	<u>Test G</u>		
	90 Day Humidity Chamber Test		
	Brass-Plated Steel Cord ^d		
	Kg/cm	23.81	19.82
20	% rubber coverage	75	65
	% retention	82.8	79.3
	<u>Test H</u>		
	120 Day Humidity Chamber Test		
	Brass-Plated Steel Cord ^d		
25	Kg/cm	20.72	23.04
	% rubber coverage	70-75	85
	% retention	72.1	92.2
	<u>Test I</u>		
	150 Day Humidity Chamber Test		
30	Brass-Plated Steel Cord ^d		
	Kg/cm	12.32	17.86
	% rubber coverage	15	75-80
	% retention	42.9	71.4
35	a) T-adhesion pads cured 30 minutes at 149° C and tested at 110° C.		
	b) T-adhesion pads cured 30 minutes at 149° C, heat aged in a forced air oven for 2 days at 121° C and tested at 110° C.		

- c) T-adhesion pads cured 30 minutes at 149° C, steam bomb aged 1 hour at 149° C and tested at 110° C.
- 5 d) T-adhesion pads cured 30 minutes at 149° C, aged in humidity chamber at 90% relative humidity and 35° C and tested at 110° C.

10 As can be determined from Table III, short term adhesion to brass-plated steel cord was slightly better with Manobond C-16 than the nickel adipate complex in the initial, unaged condition, although thereafter, throughout Tests B and C, the cured rubber skim stock containing the nickel adipate complex gave better short term adhesion

15 properties. During long term humidity aging, the Manobond additive performed slightly better until after 90 days of aging at which time the cured rubber skim stock containing the nickel adipate complex provided better long term adhesion properties.

20 Based on the foregoing results reported in Tables I to III, we consider the presence of cobalt or nickel complexes in a rubber skim stock to be effective in promoting adhesion between the rubber skim stock and metallic reinforcement. As demonstrated hereinabove, the test wire

25 used to practice our invention with dicarboxylic complexes of cobalt can be, for example, brass-plated wire, i.e., 70% Cu, 30% Zn; zinc-plated or bright steel. The wire can be in the form of a strand, mat, web, ply or braid. For the nickel complexes, adhesion properties are good with

30 brass-plated steel.

The present invention also finds utility in, for example, brassed metal-rubber articles such as motor mounts, cutless bearings, torsilastic springs, power belts, printing rolls, metal wire reinforced or braided hose,

35 electrical deicers, shoe heels and wherever it is desired to secure rubber to metal or provide a flexible and strong, thermally stable bond between the same.

Thus, it can be seen that the disclosed invention carries out the objects set forth hereinabove. As will be apparent to those skilled in the art, the composition of the rubber skim stock can be varied within the scope of our
5 total specification disclosure by the selection of the various metal dicarboxylate complexes as well as the amounts thereof, and it is believed that the preparation and use of these according to the preferred method of the invention can be determined without departing from the
10 spirit of the invention herein disclosed and described, the scope of the invention being limited solely by the scope of the attached claims.

It is to be understood that variations of the disclosure fall within the scope of the claimed invention
15 and that the subject invention is not to be limited by the examples set forth herein. They have been provided merely to demonstrate operability and therefore the selection of metals or dicarboxylic acids to form the complexes disclosed herein can be determined without departing from the
20 spirit of the invention herein disclosed and described. Moreover, the scope of the invention shall include all modifications and variations that fall within the scope of the attached claims.

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- 1 1. Cured rubber skim stock compositions having improved
2 metal adhesion and metal adhesion retention properties,
3 said composition comprising:
4 100 parts of a vulcanizable rubber stock; and,
5 from about 0.50 to about 10.0 parts by weight of
6 an organic complex of cobalt and a dicarboxylic acid
7 per 100 parts of the rubber component in said rubber
8 stock.
- 1 2. Cured rubber skim stock compositions, as set forth in
2 claim 1, wherein said dicarboxylic acids are selected
3 from the group consisting of aliphatic and aromatic
4 dicarboxylic acids having from two to about 20 carbon
5 atoms.
- 1 3. Cured rubber skim stock compositions, as set forth in
2 claim 2, wherein said cobalt complex is cobalt adipate.
- 1 4. Cured rubber skim stock compositions, as set forth in
2 claim 2, wherein said cobalt complex is cobalt
3 azelate.
- 1 5. Cured rubber skim stock compositions, as set forth in
2 claim 2, wherein said metal is present in a metallic
3 reinforcing cord selected from the group consisting of
4 steel cord, brass-plated steel cord and zinc-plated
5 steel cord.
- 1 6. Cured rubber skim stock compositions having improved
2 metal adhesion and metal adhesion retention properties,
3 said composition comprising:
4 100 parts of a vulcanizable rubber stock; and,
5 from about 0.50 to about 12.0 parts by weight
6 of an organic complex of nickel and a dicarboxylic
7 acid per 100 parts of the rubber component in said
8 rubber skim stock.

- 1 7. Cured rubber skim stock compositions, as set forth in
2 claim 6, wherein said dicarboxylic acids are selected
3 from the group consisting of aliphatic and aromatic
4 dicarboxylic acids having from two to about 20 carbon
5 atoms.
- 1 8. Cured rubber skim stock compositions, as set forth in
2 claim 7, wherein said nickel complex is nickel adipate.
- 1 9. Cured rubber skim stock compositions, as set forth in
2 claim 7, wherein said metal is present in a metallic
3 reinforcing cord comprising brass-plated steel cord.
- 1 10. A tire having metallic reinforcing elements embedded
2 in vulcanized rubber skim stock, said skim stock being
3 characterized by having incorporated therein:
4 from about 0.50 to about 10.0 parts by weight of
5 an organic complex of cobalt and a dicarboxylic acid
6 per 100 parts of the rubber component in said rubber
7 skim stock.
- 1 11. A tire, as set forth in claim 10, wherein the metallic
2 reinforcing elements are selected from the group
3 consisting of steel cord, brass-plated steel cord and
4 zinc-plated steel cord and wherein said dicarboxylic
5 acids are selected from the group consisting of ali-
6 phatic and aromatic dicarboxylic acids having from two
7 to about 20 carbon atoms.
- 1 12. A tire, as set forth in claim 11, wherein said cobalt
2 complex is cobalt adipate.
- 1 13. A tire, as set forth in claim 11, wherein said cobalt
2 complex is cobalt azelate.
- 1 14. A tire having metallic reinforcing elements embedded
2 in vulcanized rubber skim stock, said skim stock being
3 characterized by having incorporated therein:

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4 from about 0.50 to about 12.0 parts by weight
5 of an organic complex of nickel and a dicarboxylic
6 acid per 100 parts of the rubber component in said
7 rubber skim stock.

1 15. A tire, as set forth in claim 14, wherein the metallic
2 reinforcing elements comprise brass-plated steel cord
3 and wherein said dicarboxylic acids are selected from
4 the group consisting of aliphatic and aromatic
5 dicarboxylic acids having from two to about 20 carbon
6 atoms.

1 16. A tire, as set forth in claim 15, wherein said nickel
2 complex is nickel adipate.



European Patent
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EUROPEAN SEARCH REPORT

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Application number

EP 82 10 1389

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
D, A	US-A-2 912 355 (R.J.FORMANCK et al.) *Claim 1; column 2, lines 30-31 and 35*		C 08 J 5/10 C 08 L 21/00 C 08 K 5/09
A	FR-A-2 198 830 (YOKOHAMA RUBBER) *Claim 1* & GB - A - 1 389 800		
A	DE-A-2 363 655 (BRIDGESTONE) *Claim 1* & US - A - 3 903 026 (Cat. D)		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
			C 08 J C 08 L C 08 K B 29 H
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 04-06-1982	Examiner VAN HUMBEECK F.W.C.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			